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(54) **Electron donors for improved olefin polymerization**

Elektrondonor zur verbesserten Olefinpolymerisation

Donneurs d'électrons pour la polymérisation améliorée d'oléfines

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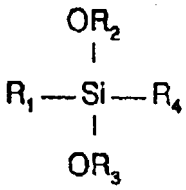
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Description

BACKGROUND

TECHNICAL FIELD:

[0001] The present invention provides a catalyst system for the polymerization of olefins that include the combination of a specific titanium catalyst with an electron donor compound of the formula:



wherein R_1 is an alkyl group containing a tertiary carbon atom attached to the silicon atom; R_2 and R_3 are alkyl or aryl groups; and R_4 is an alkyl with a tertiary carbon atom attached to the silicon atom, R_1 and R_4 are the same or different.

DESCRIPTION OF PRIOR ART:

[0002] Catalyst systems for the polymerization of olefins are well known in the art. Typically, these systems include a Ziegler-Natta type polymerization catalyst; a co-catalyst, usually an organoaluminum compound; and an electron donor compound. Examples of such catalyst systems are shown in the following U.S. Patents: 4,107,413; 4,294,721; 4,439,540; 4,115,319; 4,220,554; 4,460,701; 4,562,173 and in the European Patents EP-A-0452916, EP-A-0439622 and EP-A-0250229. These are just a few of the scores of issued patents relating to catalysts and catalyst systems designed primarily for the polymerization of propylene and ethylene.

[0003] A Ziegler-Natta type polymerization catalyst is basically a complex derived from a halide of a transition metal, for example, titanium, chromium or vanadium with a metal hydride and/or a metal alkyl that is typically an organoaluminum compound. The catalyst is usually comprised of a titanium halide supported on a magnesium compound complexed with an alkylaluminum.

[0004] The development of these polymerization catalysts has proceeded seemingly in generations of catalysts. The catalyst disclosed in the patents referenced above are considered by most to be third generation catalysts. With each new generation of catalysts, the catalyst properties have improved. Particularly, the efficiencies of the catalysts, as expressed in kilograms of polymer product per gram of catalyst in two hours, have increased from the 1-3 range to the 10-12 range and beyond. Catalysts have been developed that not only have higher efficiencies but also retain their activity over a longer period of time, thus being able to produce more polymer product over the life of the catalyst. Any increase in the efficiency and life of the catalyst leads to lower costs due to lower catalyst consumption, and it also lowers the capital expenditures in building and operating a plant as the size of the reactors are lowered for specific plant capacities and the reactor residence time is lowered. A higher efficiency also leads to a cleaner polymer product thereby avoiding the need to wash or treat the product to remove catalyst ash residuals.

[0005] In addition to the improved catalysts, improved activation methods have also lead to increases in the catalyst efficiency. A most recent discovery includes a process for pre-polymerizing the catalyst just prior to introducing the catalyst into the reaction zone. This process is disclosed in U.S. Patent No. 4,767,735.

[0006] In addition to the development of new catalysts and new reaction processes, a discovery of a more appropriate co-catalyst or electron donor to go with the new generation of catalysts in forming a total catalyst system would be of great benefit to the polymerization art especially if it leads to dramatic increases in the efficiency of the catalyst system and to improved quality control of the polymer product. In such a total catalyst system, a co-catalyst activates the catalyst and provides the initiation of a polymer chain. The co-catalyst that works well with the new generation catalysts is an organoaluminum compound, most typically triethylaluminum (TEAl) or another trialkyialuminum. Examples of other useful organoaluminum compounds include an alkylaluminum dihalide, a trialkoxyaluminum, a dialkylaluminum halide, and a triisobutylaluminum.

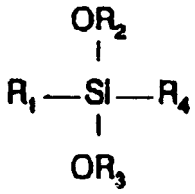
[0007] An electron donor compound is used in the polymerization reaction to reduce the atactic form of the polymer thereby giving control of and increasing the production of isotactlc polymers. Although a broad range of compounds are known generally as electron donors, a particular catalyst may have a specific compound or group of compounds with which it is especially compatible. Work disclosed in Makromol, Chem., Härkönen et al, vol. 192, p. 2857 (1991) and in

"Catalytic Olefin Polymerization"(Keli, T., Soga, K., Eds., Elsevier:New York, 1990) Härkönen et al, p. 87, has shown that some effects of the donor can be influenced by its structure and suggests that a high performance alkoxysilane donor will contain at least two small alkoxy groups, preferably methoxy, and one or two branched alkyl groups. Other work suggested that a good donor preferably has a dimethoxy structure with a bulky alkyl or cycloalkyl group containing at least one secondary or tertiary carbon, but that the second alkyl group should contain a primary carbon. One such group of electron donors are disclosed in U.S. Patent No. 4,927,797.

[0008] The present invention comprises another such discovery of an appropriate type of electron donor which gives significant increases in catalyst efficiency as well as improved control of the isotactic index of the desired polymer product and other properties of the product would be highly advantageous. It has been surprisingly discovered that a specific group of silane compounds serving as electron donors in combination with a particular type of catalyst results In significant increases in catalyst efficiency over the previously known efficiencies for this particular type of catalyst as well as other known catalyst systems.

SUMMARY OF THE INVENTION

[0009] The present invention provides a catalyst system for the polymerization of olefins according to claim 1 wherein the system includes the combination of a particular type of catalyst with a specific group of electron donor compounds which results in significant increases in the efficiency of the catalyst and improved control of the properties of the polymer product. The catalyst is a new generation catalyst comprising a complex of a dialkoxy magnesium and a titanium halide. The electron donor is selected from a silane compound of the following formula:



wherein R_1 is an alkyl group containing a tertiary carbon atom attached to the silicon; R_2 and R_3 are alkyl or aryl groups; and R_4 is an alkyl group with a tertiary carbon atoms attached to the silicon atom, R_1 and R_4 being the same or different. In a preferred embodiment, R_1 is a tertiary alkyl group of 4-13 carbon atoms, more preferably, 4-7 carbon atoms; R_2 and R_3 are methyl, ethyl, propyl, or butyl groups and not necessarily the same; and R_4 is a tertiary alkyl group of 4-13 carbon atoms; preferably R_1 and R_4 ar the same; R_1 and R_4 are most preferably t-butyl with R_1 and R_4 being the same; the preferred electron donor is di-t-butyldimethoxysilane (DTDS). In addition, the system may contain an organoaluminum compound which acts as a co-catalyst.

[0010] The cocatalyst is selected from the group consisting of an alkylaluminum, an alkylaluminum dihalide, a trialkoxyaluminum, a dialkylaluminum halide and a triisobutylaluminum. A preferred co-catalyst is a trialkylaluminum, most preferably triethylaluminum (TEAl).

[0011] The invention also provides a catalyst system as described above, wherein the system is capable of polymerizing an olefin monomer with a catalyst efficiency of about 25 kilograms of polymer product per gram of catalyst in one hour. Particular catalyst systems included in the invention may show somewhat lower efficiencies. Further, the catalyst system may be characterized by an efficiency of over 25 kg/g-cat • h while the Si/Ti ratio defined by the mole ratio of the silane electron donor and the titanium component of the catalyst varies within the range 4-200 and by an isotactic capacity such that the system produces a polymer product in which the xylene solubles are controlled at about 3.00 wt% or less of the polymer product while the Si/Ti mole ratio varies down to 4. Additionally, the catalyst system may be further characterized by an efficiency greater than 25 while producing a polymer product with xylene solubles of about 3.00 wt% or less.

[0012] The catalyst system may be further characterized by having an isotactic capacity such that the system produces a polymer product in which the xylene soluble atactic form may be kept at about 3.00 wt% of the product while the Si/Ti mole ratio varies up to 200. The system may be further characterized by higher molecular weight of the product.

[0013] The invention also provides a process for the polymerization of olefins. The process comprises: contacting the new generation polymerization catalyst with an organoaluminum compound, preferably with a trialkylaluminum; contacting the catalyst with an electron donor either simultaneously with or after contact with the organoaluminum, the electron donor being a silane compound as described by the formula above, pre-polymerizing the catalyst by contacting a small amount of monomer with the catalyst; and introducing the catalyst into a polymerization reaction zone containing

the organoaluminum compound, the electron donor and the monomer. The process further comprises withdrawing a polymer product in which the xylene solubles are at 3.00 wt% or less, while the Si/Ti ratio in the reaction zone is within the range 4-200.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The present invention relates to the combination of a particular group of compounds as electron donors with a particular type of catalyst for use in the polymerization of propylene. This combination results in a catalyst system that has a catalyst efficiency significantly higher than provided by previous catalyst systems as illustrated by the comparative examples included below. Further, the catalyst system of the present invention retains most of its high activity over time relative to other catalyst systems. The catalyst system also provides better control of the xylene solubles of the polymer product than with other electron donors and the particular type of catalyst These and other beneficial advantages will become more apparent from the following detailed description of the invention and the accompanying examples.

[0015] Electron donors are typically used in two ways in the formation of a Ziegler-Natta catalyst and a catalyst system. First, an internal electron donor may be used in the formation reaction of the catalyst as the transition metal halide is reacted with the metal hydride or metal alkyl. Examples of internal electron donors include: amines, amides. ethers, esters, aromatic esters, ketones, nitriles, phosphines, stibines, arsines, phosphoramides, thloethers, thioesters, aldehydes, alcoholates, and salts of organic acids. The second use for an electron donor in a catalyst system is as an external electron donor and stereoregulator in the polymerization reaction. The same compound may be used in both instances, although typically they are different. A common external electron donor is an organic silicon compound, for example, cyclohexylmethyldimethoxysilane (CMDS). A description of the two types of electron donors is provided in U.S. Patent 4,535,068.

[0016] As the present invention relates particularly to external electron donors, the term "electron donor" as used herein, refers to the external donor. The external electron donor acts as a stereoregulator to control the amount of atactic form of polymer produced. It may also increase the production of isotactic polymers. Organic silicon compounds are known in the art for use as electron donors. Examples of electron donors that are organic silicon compounds are disclosed in U.S. Patent Nos. 4,218,339; 4,395,360; 4,328,122; 4,473,660 and 4,927,797. As mentioned, a particular catalyst may produce better results when paired with a particular group of electron donors. Examples of this pairing of catalyst and electron donors are disclosed in U.S. Patent Nos. 4,562,173; 4,547,552; and 4,927,797.

[0017] It has been discovered that a particular group of electron donors does significantly enhance the catalytic properties of a specific Ziegler-Natta catalyst.

[0018] The Ziegler-Natta catalyst which is used in the present invention is a new generation, Ziegler-type titanium catalyst for the polymerization of olefins comprising a solid catalyst component obtained by (i) suspending a dialkoxy magnesium in an aromatic hydrocarbon that is liquid at normal temperatures, (ii) contacting the dialkoxy magnesium with a titanium halide and further (iii) contacting the resulting composition a second time with the titanium halide, and contacting the dialkoxy magnesium with a diester of an aromatic dicarboxylic acid at some point during the treatment with the titanium halide in (ii), as disclosed in U.S. Patent Nos. 4,927,797; 4,816,433 and 4,839,321.

[0019] Preferred aromatic hydrocarbons useful in the formation of the catalyst include benzene, xylene, ethylbenzene, propylbenzene and trimethylbenzene. A diester of phthalic acids is preferably used as the diester of the aromatic dicarboxylic acid. Examples include dimethyl phthalate, diethyl phthalate, dipropyl phthalate, diisopropyl phthalate, dibutyl phthalate, diisobutyl phthalate, diamyl phthalate, diisoamyl phthalate, methylbutyl phthalate, ethylbutyl phthalate, ethylisobutyl phthalate and ethylpropyl phthalate. Suitable titanium halides include $TiCl_4$, $TiBr_4$ and TiI_4, with $TiCl_4$ being preferred.

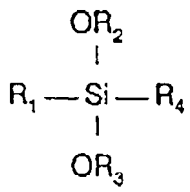
[0020] The ratios of the respective components are not critical but can vary to tailor the performance of the catalyst. However, in generally, the diester of the aromatic dicarboxylic acid is used in an amount of 0.01 to 2 g, preferably 0.1 to 1 g, per gram of the dialkoxy magnesium, and the titanium halide is used in an amount of at least 0.1 g, preferably at least 1 gram, per gram of the alkoxy magnesium. The amount of the aromatic hydrocarbon which is liquid at normal temperature should be sufficient to form a suspension.

[0021] Suspension of the dialkoxy magnesium into the aromatic hydrocarbon is performed at a temperature of from room temperature to the boiling point of the aromatic hydrocarbon used for up to 100 hours, preferably up to 10 hours. It is important that the formed suspension should not be a homogeneous solution. The contact of the suspension with the titanium halide and the contact of the composition obtained by said contact with the titanium halide are carried out at a temperature of from -20°C to the boiling point of the titanium halide used, preferably 50 to 120°C, for 10 minutes to 10 hours. The means for contacting the components is not particularly critical, so far as sufficient contact is attained among the respective components. Preferably, the contact is carried out by using a vessel provided with a stirrer.

[0022] The above-described catalyst exhibits some increase in efficiency over previously known catalysts when it is paired with a previously used electron donor, but that increase is significantly greater when the catalyst is paired with electron donors as described by the present invention. This improved efficiency is accompanied by better operational

control of the properties of the polymer product such as the xylene solubles.

[0023] The electron donors induded in the present invention are organic silicon compounds such as those described by the following formula:



wherein R_1 is an alkyl group containing a tertiary carbon atom attached to the silicon atom; R_2 and R_3 are alkyl or aryl groups; and R_4 is an alkyl group with a tertiary carbon atom attached to the silicon atom; R_1 and R_4 are the same or different.

[0024] In preferred embodiments of the invention, R_1 is a tertiary alkyl group of 4-13 carbon atoms, more preferably, 4-7 carbon atoms, R_2 and R_3 are methyl, ethyl or propyl groups, and R_4 is a tertiary alkyl group of 4-13 carbon atoms. R_2 and R_4 are preferably the same and, most preferably, are t-butyl with R_1 and R_4 being the same. The most preferred electron donor is di-t-butyldimethoxysilane (DTDS). The combination of this class of electron donors and a conventional Ziegler-Natta catalyst yields wholly unexpected results that surpass previously known catalyst systems, The electron donors as described by the present invention may be limited by the stability of the compound and the ease of handling including storage, transportation and use in the plant.

[0025] The most significant unexpected result obtained from the combination of the above-described catalyst and DTDS is the dramatic increase in the efficiency of the catalyst system as measured in kilograms of polymer product per gram of catalyst in one hour (kg/g-cat • h). The catalyst system, which includes an organo-aluminum compound, has been shown to achieve efficiencies higher than 25 kg/g-cat • h, and the efficiency can be over 25 kg/g-cat • h for Si/Ti mole ratios within the range 4-200. The optimum Si/Ti ratio in order to achieve the highest efficiency is within the range from 4 to 20 and from 100-200.

[0026] Further, the catalyst system is capable of achieving these high efficiencies over a wide range of Si/Ti ratios (4-200) while exhibiting an isotactic capacity in controlling the formation of atactic polymer, or xylene solubles, at relatively low levels. When the catalysts described herein are paired with another donor such as CMDS. the system exhibits a linear decrease in efficiency as the Si/Ti ratio approaches 200 ("sick reaction"). The present catalyst system using DTDS, however, exhibits a very consistent efficiency at Si/Ti ratios between 4 and 200 and actually increases as the Si/Ti ratio increases from 40 to 200, This consistency, as opposed to a decrease, has dramatic operational consequences. With a relationship between Si/Ti and efficiency which changes slowly and gradually, a change in the Si/Ti ratio results in only a small change in the efficiency. This allows for small fluctuations in the operation of the reactor, such as when new feed is input or operational errors occur, while still controlling the efficiency of the catalyst within a desired range. The decrease in efficiency exhibited by the CMDS system, on the other hand, leads to substantial changes in the efficiency with any fluctuation in the Si/Ti mole ratio. The consistency and even increase in efficiency of DTDS system at high Si/Ti ratios is very surprising and unexpected.

[0027] An advantage is that a highly active and stable system produces a cleaner polymer as there is more polymer produced for the same amount of catalyst ash and therefore resulting in a lower percentage of ash content in the polymer. The co-polymer product would be less corrosive, exhibit less color and be more applicable for use in electrical systems.

[0028] The present invention also provides a process for the polymerization of olefins according to claim 22 using the catalyst and the electron donors described by the above formula comprising:

a) selecting a specific Ziegler-Natta catalyst component;
b) contacting the catalyst with an organoalumlnum compound;
c) contacting the catalyst with an electron donor as described above;
d) introducing the catalyst into a polymerization reaction zone containing the organoaluminum compound, the electron donor and the monomer; and
e) extracting polymer product from the reactor.

Although the catalyst system may be used in almost any commercially known polymerization process, the preferred process of the present invention includes a pre-polymerization of the catalyst by contacting a small amount of monomer with the catalyst after the catalyst has been contacted with the electron donor. A pre-polymerization process is described in U.S. Patent Nos. 4,767,735, and 4,927,797, incorporated by reference above. As provided in those disclo-

sures, a carrier stream for the catalyst is provided, the catalyst is contacted with the co-catalyst or organoaluminum compound, the catalyst is contacted with the electron donor, the catalyst stream is contacted with a relatively small amount of the total amount of monomer to be polymerlzed, the catalyst stream passes through a tubular reactor, and the pre-polymerized catalyst and catalyst stream are introduced into the polymerization reaction zone. The electron donor may be contacted with the catalyst simultaneously with the co-catalyst. A polymer product may then be withdrawn from the reactor. In using the described catalyst with the electron donors described by the formula above, the catalyst may have an efficiency of above 25 kg/g-cat • h while the Si/Ti mole ratio in the reaction is within the range 4-200. The polymer product may also be characterized by xylene solubles at about 3.00 wt% or less.

[0029] The following Examples and Comparative Examples illustrate the present invention and its various advantages in more detail. The results are summarized in Tables 1-5. The catalyst used was prepared with the materials and processes as disclosed in U.S. Patent Nos. 4,927,797; 4,816,433 and 4,839,321.

Example 1

[0030] Prior to a polymerization run, all traces of moisture and air are expelled from the reactor by heating to a temperature over 100°C for a minimum of 30 minutes under a constant purge of dry nitrogen. Following this heating, the reactor is cooled to room temperature (25°C) under nitrogen. The reactor is stabilized at room temperature and then 16 mmoles of hydrogen and 1.0 L of propylene are added. The reactor is stirred at 1000 rpm and the temperature remains at room temperature. 1.0 mmole of TEAl and 0.02 mmole of DTDS are added to a 40 cc tubular reaction vessel. Ten milligrams of catalyst in a mineral oil suspension are added to the 40 cc reaction cylinder. The TEAl and DTDS are allowed to pre-contact approximately five minutes, and the catalyst is allowed to pre-contact the TEAl and DTDS mixture for approximately two minutes. The tubular reaction vessel is then attached to an entry point on the reactor and the catalyst is flushed into the reactor with room temperature liquid propylene. The reactor temperature is ramped up to 70°C. The total amount of liquid propylene present in the reactor is about 1.2 L. The polymerization reaction is allowed to proceed for one hour, at which point it is terminated by venting the excess propylene and cooling the reactor to room temperature. The reactor is then opened to collect the polymer product which is dried and analyzed. The efficiency of the catalyst was determined from the mass yield of polymer for the known amount of catalyst used. The efficiency is reported in kilograms of polymer product per gram of catalyst per hour. The Si/Ti mole ratio was calculated from the molar amount of DTDS used divided by the molar amount of catalyst. The xylene solubles were measured by dissolving the polymer in hot xylene, cooling the solution to 0°C and precipitating out the isotactic form. The xylene solubles are the wt% of the polymer that was soluble in the cold xylene. In addition, the bulk density of the polymer product was measured and calculated using standard techniques. The results are shown in Table 1.

Examples 2-11

[0031] The procedures of Example 1 were repeated except that the total amount of DTDS was varied as indicated in Table 1 from 0.05 mmoles to 1.00 mmoles. This varied the SI,Ti ratio from 4 to 200 and illustrates the effect of the Si/Ti ratio on the efficiency and on the xylene solubles. The results are tabulated in Table 1.

Comparative Examples 1-5

[0032] The procedure of Example 1 were repeated except that CMDS was substituted for DTDS as the electron donor. The results are shown in Table 2.

TABLE 1

DTDS SYSTEM									
Example	TEAl mmol	DTDS mmol	Si/Ti	Catalyst mg	H_2 mmol	Yield g	Efficiency Kg/g-cat • h	Bulk Density[a)]	Xylene Soluble wt%
1	1	0.02	4	10	16	393	39.3	0.44	3.3
2	1	0.05	10	10	16	346	34.6	0.48	2.8
3	1	0.05	10	10	16	319	31.9	0.47	2.8
4	1	0.10	20	10	16	257	25.7	0.46	2.6
5	1	0.10	20	10	16	268	26.8	0.46	2.5
6	1	0.20	40	10	16	263	26.3	0.46	2.1
7	1	0.50	100	10	16	336	33.6	0.47	1.7
8	1	0.50	100	10	16	334	33.4	0.46	2.0
9	1	1.00	200	10	16	325	32.5	0.47	2.3
10	1	1.00	200	10	16	304	30.4	0.46	1.8
11	1	0.05	10	10	8	296	29.6	0.45	2.8
12	1	0.05	10	10	32	403	40.3	0.47	2.8

a) Bulk density is given in grams per cubic centimeter for the polymer fluff.

TABLE 2

Comparative Example	TEAl mmol	CMDS mmol	Si/Ti	Catalyst mg	H_2 mmol	Yield g	Efficiency Kg/g-cat • h	Bulk Density[a)]	Xylene Solubles wt%
1	1	0.05	10	10	16	327	32.7	0.48	1.7
2	1	0.10	20	10	16	321	32.1	0.48	1.6
3	1	0.20	40	10	16	328	32.8	0.47	1.3
4	1	0.50	100	10	16	232	23.2	0.48	1.3
5	1	1.00	200	10	16	115	11.5	0.42	1.6
6	1	0.05	10	10	8	264	26.4	0.47	1.8
7	1	0.05	10	10	32	313	31.3	0.48	1.7

a) Bulk density is given in grams per cubic centimeter for the polymer fluff.

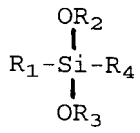
[0034] As shown in Table 1, the efficiency is greater than 25 kg/g-cat • 1h for Si/Ti ratios within the range from about 4 to about 20 and it increases as the Si/Ti ratio increases from about 40 to about 200, reaching a maximum at some point at about 4 and at about 100 Si/Ti. The DTDS system is capable of easily achieving efficiencies greater than 25 kg/g-cat • 1h. Also, as seen from the results shown In Table 1, the xylene solubles are controlled within a narrow range as the Si/Ti ratio varies from 4-200. The relationship is nearly linear with a small, gradual slope. As discussed, these relationships of the properties of the polymer and the Si/Ti ratio are very advantageous in allowing some fluctuations In the operation of the reactor and/or some errors without significantly changing the properties of the product. It also allows particular specifications for a product to be achieved more easily with a broader range of reactor parameters.

The results are shown in Table 1.

Claims

1. A catalyst system for the polymerization and copolymerization of olefins comprising:

(a) a Ziegler-Natta catalyst component comprising a solid catalyst component prepared by: (i) suspending a dialkoxy magnesium in an aromatic hydrocarbon that is liquid at normal temperatures, (ii) contacting the dialkoxy magnesium with a titanium halide and further contacting the resulting composition a second time with the titanium halide, and (iii) contacting the dialkoxy magnesium with a diester of an aromatic dicarboxylic acid at some point during the treatment with the titanium halide in (ii); and
(b) an external electron donor described by the formula :



wherein R_1 is an alkyl group containing a tertiary carbon atom attached to the silicon atom; R_2 and R_3 are each independently an alkyl or aryl group; and R_4 is an alkyl group with a tertiary carbon atom attached to the silicon atom, R_1 and R_4 are the same or different.

2. The catalyst system of Claim 1 wherein R_1 and R_4 are tertiary alkyls of 4-13 carbon atoms.

3. The catalyst system of Claim 2 wherein R_1 and R_4 are tertiary alkyls of 4-7 carbon atoms.

4. The catalyst system of Claim 1 wherein R_1 and R_4 are the same.

5. The catalyst system of Claim 4 wherein R_1 and R_4 are t-butyl groups.

6. The catalyst system of Claim 1 wherein R_2 and R_3 are selected from the group consisting of methyl, ethyl, propyl and butyl groups.

7. The catalyst system of Claim 1 further comprising : (c) an organoaluminum compound.

8. The catalyst system of Claim 7 wherein the organoaluminum compound is selected from the group consisting of a trialkylaluminum, an alkylaluminum dihalide and a dialkylaluminum halide.

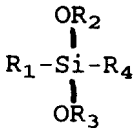
9. The catalyst system of Claim 8 wherein the organoaluminum compound is triethylaluminum.

10. The catalyst system of Claim 1 or Claim 8 wherein the electron donor is di-t-butyl- dimethoxysilane.

11. A catalyst system for the polymerization and copolymerization of olefins, said system comprising :

(a) a Ziegler-Natta catalyst component comprising a solid catalyst component prepared by: (i) suspending a dialkoxy magnesium in an aromatic hydrocarbon that is liquid at normal temperatures, (ii) contacting the dialkoxy magnesium with a titanium halide and further contacting the resulting composition a second time with the titanium halide, and (iii) contacting the dialkoxy magnesium with a diester of an aromatic dicarboxylic acid at some point during the treatment with the titanium halide in (ii); and

(b) an external electron donor described by the formula :



wherein R_1 is an alkyl group containing a tertiary carbon atom attached to the silicon atom; R_2 and R_3 are each independently an alkyl or aryl group; and R_4 is an alkyl group with a tertiary carbon atom attached to the silicon atom; R_1 and R_4 are the same or different;

(c) an organoaluminum compound;
said system being characterized by a catalyst efficiency of over 25 kilograms of polymer product per gram of catalyst in one hour as the mole ratio Si/Ti as derived from the Si in compound (b) to the Ti from compound (a) is within the range of 4-200.

12. The system of Claim 11 wherein the system is further characterized by a polymer product in which the xylene solubles measured by dissolving the polymer in hot xylene, cooling the solution to 0°C and precipitating out the isotactic form, the xylene solubles being the wt% of the polymer that was soluble in the cold xylene, are controlled at 3.00 wt% or less of the polymer product while the Si/Ti mole ratio is within the range of 4-200.

13. The system of Claim 11 wherein R_1 and R_4 are tertiary alkyls of 4-13 carbon atoms.

14. The system of Claim 13 wherein R_1 and R_4 are tertiary alkyls of 4-7 carbon atoms.

15. The system of Claim 11 wherein R_1 and R_4 are the same.

16. The system of Claim 15 wherein R_1 and R_4 are t-butyl groups.

17. The system of Claim 11 wherein R_2 and R_3 are selected from the group consisting of methyl, ethyl, propyl and butyl groups.

18. The system of Claim 11 wherein the catalyst is prepolymerized.

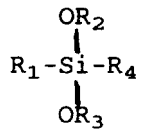
19. The system of Claim 11 wherein the organoaluminum compound is selected from the group consisting of a trialkylaluminum, an alkylaluminum dihalide and a dialkylaluminum halide.

20. The system of Claim 11 wherein the electron donor is selected from the group consisting of di-t-butyldimethoxylane.

21. The system of Claim 18 wherein the organoaluminum compound is triethylaluminum.

22. A process for the polymerization of olefins, comprising :

(a) selecting a Ziegler-Natta catalyst component comprising a solid catalyst component obtained by (i) suspending a dialkoxy magnesium in an aromatic hydrocarbon that is liquid at normal temperatures, (ii) contacting the dialkoxy magnesium with a titanium halide and further contacting the resulting composition a second time with the titanium halide, and (iii) contacting the dialkoxy magnesium with a diester of an aromatic dicarboxylic acid at some point during the treatment with the titanium halide in (ii);
(b) contacting the catalyst component with an organoaluminum compound to activate the catalyst;
(c) contacting said catalyst with an external electron donor either simultaneously with or after step (b), said electron donor being described by the formula :



wherein R_1 is an alkyl group containing a tertiary carbon atom attached to the silicon atom; R_2 and R_3 are each independently an alkyl or aryl group; and R_4 is an alkyl group with a tertiary carbon atom attached to the silicon atom; R_1 and R_4 are the same or different;

(d) pre-polymerizing said catalyst by contacting a small amount of monomer with said catalyst; and

(e) introducing said catalyst into a polymerization reaction zone containing said organoaluminum compound, said electron donor and said monomer.

23. The process of Claim 22 wherein said organoaluminum compound is triethylaluminum.

24. The process of Claim 22 wherein R_1 and R_4 are tertiary alkyls of 4-13 carbon atoms.

25. The process of Claim 24 wherein R_1 and R_4 are tertiary alkyls of 4-7 carbon atoms.

26. The process of Claim 22 wherein R_1 and R_4 are the same.

27. The process of Claim 22 wherein R_1 and R_4 are t-butyl groups.

28. The process of Claim 22 wherein said monomer is propylene.

29. The process of Claim 22 wherein said electron donor is di-t-butyl-dimethoxysilane.

30. The process of Claim 22 wherein said process is characterized by a catalyst efficiency of over 25 kg of polymer product per gram of catalyst in one hour with the mole ratio of Si/Ti from the silicon electron donor and the catalyst within the range of 4-200.

31. The process of Claim 22 wherein said process is characterized by producing a polymer product in which the xylene solubles measured by dissolving the polymer in hot xylene, cooling the solution to 0°C and precipitating out the isotactic form, the xylene solubles being the wt% of the polymer that was soluble in the cold xylene, is at 3.00 wt % or less of the polymer product.

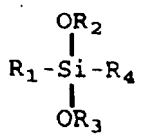
32. The process of Claim 22 further comprising the addition of a second monomer so as to form a copolymer.

Patentansprüche

1. Katalysatorsystem für die Polymerisation und Copolymerisation von Olefinen, umfassend:

(a) eine herkömmliche Ziegler-Natta Katalysatorkomponente, enthaltend eine feste Katalysatorkomponente, hergestellt durch (i) Suspendieren eines Dialkoxymagnesiums in einem aromatischen Kohlenwasserstoff, der bei normalen Temperaturen flüssig ist, (ii) in Kontakt bringen des Dialkoxymagnesiums mit einem Titanhalogenid und ferner in Kontakt bringen der sich ergebenden Zusammensetzung ein Zweites Mal mit dem Titanhalogenid, und (iii) in Kontakt bringen des Dialkoxymagnesiums mit einem Diester einer aromatischen Dicarbonsäure an einem Punkt während der Behandlung mit dem Titanhalogenid in (ii), und

(b) einen externen Elektronendonor, beschrieben durch die Formel:



wobei R_1 eine Alkylgruppe ist, die ein tertiäres Kohlenstoffatom, angefügt an das Siliciumatom, enthält, R_2 und R_3 sind jeweils unabhängig eine Alkyl- oder Arylgruppe, und R_4 ist eine Alkylgruppe mit einem tertiären Kohlenstoffatom, angefügt an das Siliciumatom, R_1 und R_4 sind gleich oder unterschiedlich.

2. Katalysatorsystem nach Anspruch 1, wobei R_1 und R_4 tertiäre Alkyle mit 4-13 Kohlenstoffatomen sind.

3. Katalysatorsystem nach Anspruch 2, wobei R_1 und R_4 tertiäre Alkyle mit 4-7 Kohlenstoffatomen sind.

4. Katalysatorsystem nach Anspruch 1, wobei R_1 und R_4 gleich sind.

5. Katalysatorsystem nach Anspruch 4, wobei R_1 und R_4 t-Butylgruppen sind.

6. Katalysatorsystem nach Anspruch 1, wobei R_2 und R_3 aus der Gruppe bestehend aus Methyl-, Ethyl-, Propyl- und Butylgruppen ausgewählt sind.

7. Katalysatorsystem nach Anspruch 1, ferner umfassend: (c) eine Organoaluminiumverbindung.

8. Katalysatorsystem nach Anspruch 7, wobei die Organoaluminiumverbindung aus der Gruppe bestehend aus einem Trialkylaluminium, einem Alkylaluminiumdihalogenid und einem Dialkylaluminiumhalogenid ausgewählt ist.

9. Katalysatorsystem nach Anspruch 8, wobei die Organoaluminiumverbindung Triethylaluminium ist.

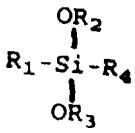
10. Katalysatorsystem nach Anspruch 1 oder Anspruch 8, wobei der Elektronendonor Di-t-Butyl-dimethoxysilan ist.

11. Katalysatorsystem für die Polymerisation und Copolymerisation von Olefinen, wobei das System umfaßt:

(a) eine herkömmliche Ziegler-Natta-Katalysatorkomponene und umfassend eine feste Katalysatorkomponente, hergestellt durch

(i) Suspendieren eines Dialkoxymagnesiums in einem aromatischen Kohlenwasserstoff, der flüssig bei normalen Temperaturen ist, (ii) in Kontakt bringen des Dialkoxymagnesiums mit einem Titanhalogenid und ferner in Kontakt bringen der sich ergebenden Zusamensetzung ein zweites Mal mit dem Titanhalogenid und (iii) in Kontakt bringen des Dialkoxymagnesiums mit einem Diester einer aromatischen Dicarbonsäure an irgendeinem Punkt während der Behandlung mit dem Titanhalogenid in ii) und

(b) einen externen Elektronendonor, beschrieben durch die Formel:



wobei R_1 eine Alkylgruppe ist, die ein tertiäres Kohlenstoffatom, angefügt an das Siliciumatom, enthält, R_2 und R_3 sind jeweils unabhängig eine Alkyl- oder Arylgruppe, und R_4 ist eine Alkylgruppe mit einem tertiären Kohlenstoffatom, angefügt an das Siliciumatom, R_1 und R_4 sind gleich oder unterschiedlich,
(c) eine Organoaluminiumverbindung, wobei das System gekennzeichnet ist durch eine Katalysatorwirksamkeit von über 25 Kilogramm Polymerprodukt pro Gramm Katalysator in einer Stunde, wenn das Molverhältnis Si/Ti, abstammend von dem Si in Verbindung (b) zu dem Ti von Verbindung (a), in dem Bereich von 4-200 ist.

12. System nach Anspruch 11, wobei das System ferner gekennzeichnet ist durch ein Polymerprodukt, in dem die xylollöslichen Stoffe, gemessen durch Lösen des Polymeren in heißem Xylol, Kühlen der Lösung auf 0°C und Herausfällen der isotaktischen Form, wobei die xylollöslichen Stoffe die Gew.% des Polymeren sind, das in dem kalten Xylol löslich war, kontrolliert werden bei 3,00 Gew.% oder weniger des Polymerprodukts, während das Si/Ti Molverhältnis in dem Bereich von 4-200 ist.

13. System nach Anspruch 11, wobei R_1 und R_4 tertiäre Alkyle mit 4-13 Kohlenstoffatomen sind.

14. System nach Anspruch 13, wobei R_1 und R_4 tertiäre Alkyle mit 4-7 Kohlenstoffatomen sind.

15. System nach Anspruch 11, wobei R_1 und R_4 gleich sind.

16. System nach Anspruch 15, wobei R_1 und R_4 t-Butylgruppen sind.

17. System nach Anspruch 11, wobei R_2 und R_3 aus der Gruppe bestehend aus Methyl-, Ethyl-, Propyl- und Butylgruppen ausgewählt sind.

18. System nach Anspruch 11, wobei der Katalysator vorpolymerisiert ist.

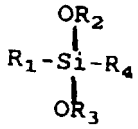
19. System nach Anspruch 11, wobei die Organoaluminiumverbindung aus der Gruppe bestehend aus einem Trialkylaluminium, einem Alkylaluminiumdihalogenid und einem Dialkylaluminiumhalogenid ausgewählt ist.

20. System nach Anspruch 11, wobei der Elektronendonor aus der Gruppe bestehend aus Di-t-Butyldimethoxysilan ausgewählt ist.

21. System nach Anspruch 18, wobei die Organoaluminiumverbindung Triethylaluminium ist.

22. Verfahren für die Polymerisation von Olefinen, umfassend:

(a) Auswählen einer herkömmlichen Ziegler-Natta-Katalysatorkomponente, umfassend eine feste Katalysatorkomponente, erhalten durch (i) Suspendieren eines Dialkoxymagnesiums in einem aromatischen Kohlenwasserstoff, der bei normalen Temperaturen flüssig ist, (ii) in Kontakt bringen des Dialkoxymagnesiums mit einem Titanhalogenid und ferner in Kontakt bringen der sich ergebenden Zusammensetzung ein zweites Mal mit dem Titanhalogenid, und (iii) in Kontakt bringen des Dialkoxymagnesiums mit einem Diester einer aromatischen Dicarbonsäure an einem Punkt während der Behandlung mit dem Titanhalogenid in (ii),
(b) in Kontakt bringen der Katalysatorkomponente mit einer Organoaluminiumverbindung unter Aktivieren des Katalysators,
(c) in Kontakt bringen des Katalysators mit einem externen Elektronendonor entweder gleichzeitig mit oder nach Stufe (b), wobei der Elektronendonor durch die Formel beschrieben ist



wobei R_1 eine Alkylgruppe ist, die ein tertiäres Kohlenstoffatom, angefügt an das Siliciumatom, enthält, R_2 und R_3 sind jeweils unabhängig eine Alkyl- oder Arylgruppe, und R_4 ist eine Alkylgruppe mit einem tertiären Kohlenstoffatom, angefügt an das Siliciumatom, R_1 und R_4 sind gleich oder unterschiedlich,
(d) Vorpolymerisieren des Katalysators durch in Kontakt bringen einer geringen Menge von Monomer mit dem Katalysator, und
(e) Einführen des Katalysators in eine Polymerisationsreaktionszone, die die Organoaluminiumverbindung, den Elektronendonor und das Monomer enthält.

23. Verfahren nach Anspruch 22, wobei die Organoaluminiumverbindung Triethylaluminium ist.

24. Verfahren nach Anspruch 22, wobei R_1 und R_4 tertiäre Alkyle mit 4-13 Kohlenstoffatomen sind.

25. Verfahren nach Anspruch 24, wobei R_1 und R_4 tertiäre Alkyle mit 4-7 Kohlenstoffatomen sind.

26. Verfahren nach Anspruch 22, wobei R_1 und R_4 gleich sind.

27. Verfahren nach Anspruch 22, wobei R_1 und R_4 t-Butylgruppen sind.

28. Verfahren nach Anspruch 22, wobei das Monomer Propylen ist.

29. Verfahren nach Anspruch 22, wobei der Elektronendonor Di-t-Butyldimethoxysilan ist.

30. Verfahren nach Anspruch 22, wobei das Verfahren durch eine Katalysatorwirksamkeit von über 25 kg Polymerprodukt pro Gramm Katalysator in einer Stunde mit dem Molverhältnis von Si/Ti aus dem Siliciumelektronendonor und dem Katalysator in dem Bereich von 4-200 gekennzeichnet ist.

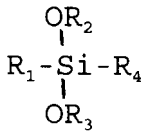
31. Verfahren nach Anspruch 22, wobei das Verfahren gekennzeichnet ist durch Herstellen eines Polymerprodukts, bei dem die xylollösliche Stoffe, gemessen durch Lösen des Polymeren in heißem Xylol, Kühlen der Lösung auf 0°C und Herausfällen der isotaktischen Form, wobei die xylollöslichen Stoffe die Gew.% des Polymeren sind, das in dem kalten Xylol löslich war, bei 3,00 Gew.% oder weniger des Polymerprodukts sind.

32. Verfahren nach Anspruch 22, ferner umfassend die Zugabe eines zweiten Monomeren, wodurch ein Copolymer gebildet wird.

Revendications

1. Un système de catalyseur pour la polymérisation et copolymérisation d'oléfines comprenant:

(a) un composant de catalyseur de Ziegler-Natta habituel comprenant un composant de catalyseur solide préparé par: (i) mettre en suspension un dialkoxy magnésium dans un hydrocarbure aromatique qui est liquide aux températures normales, (ii) mettre en contact le dialkoxy magnésium avec un halogénure de titane et mettre en outre en contact la composition résultante une deuxième fois avec l'halogénure de titane, et (iii) mettre en contact le dialkoxy magnésium avec un diester d'un acide aromatique dicarboxylique à un certain moment pendant le traitement avec l'halogénure de titane au cours de (ii); et
(b) un donneur d'électrons externes décrit par la formule:



où R_1 est un groupe alkyle contenant un atome de carbone tertiaire fixé à un atome de silicium; R_2 et R_3 sont chacun indépendamment un groupe alkyle ou aryle; et R_4 est un groupe alkyle avec un atome de carbone tertiaire fixé sur un atome de silicium, R_1 et R_4 sont identiques ou différents.

2. Le système de catalyseur selon la revendication 1 où R_1 et R_4 sont des alkyles tertiaires de 4 à 13 atomes de carbone.

3. Le système de catalyseur selon la revendication 2 où R_1 et R_4 sont des alkyles tertiaires de 4 à 7 atomes de carbone.

4. Le système de catalyseur de la revendication 1 dans lequel R_1 et R_4 sont identiques.

5. Le système de catalyseur de la revendication 4 dans lequel R_1 et R_4 sont des groupes t-butyles.

6. Le système de catalyseur de la revendication 4 dans lequel R_1 et R_3 sont choisis dans le groupe comprenant les groupes méthyle, éthyle, propyle et butyle.

7. Le système de catalyseur de la revendication 1 comprenant en outre: (c) un composé d'organoaluminium.

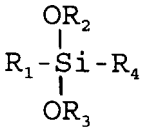
8. Le système de catalyseur de la revendication 7 dans lequel le composé d'organoaluminium est choisi dans le groupe consistant en trialkylaluminium, un dihalogénure d'alkylaluminium et un halogénure de dialkylaluminium.

9. Le système de catalyseur de la revendication 8 dans lequel le composé d'organoaluminium est le triéthylaluminium.

10. Le système de catalyseur de la revendication 1 ou de la revendication 8 dans lequel le donneur d'électrons est le di-t-butyl-diméthoxysilane.

11. Un système de catalyseur pour la polymérisation et la copolymérisation d'oléfines, ce système comprenant:

(a) un composant de catalyseur de Ziegler-Natta habituel et comprenant un composant de catalyseur solide préparé par: (i) mettre en suspension un dialkoxy magnésium dans un hydrocarbure aromatique qui est liquide aux températures normales, (ii) mettre en contact le dialkoxy magnésium avec un halogénure de titane et mettre en outre en contact la composition résultante une deuxième fois avec l'halogénure de titane, et (iii) mettre en contact le dialkoxy magnésium avec un diester d'un acide aromatique dicarboxylique à un certain moment pendant le traitement avec l'halogénure de titane au cours de (ii); et
(b) un donneur d'électrons externes décrit par la formule:



où R_1 est un groupe alkyle contenant un atome de carbone tertiaire fixé à un atome de silicium; R_2 et R_3 sont chacun indépendamment un groupe alkyle ou aryle; et R_4 est un groupe alkyle avec un atome de carbone tertiaire fixé sur un atome de silicium; R_1 et R_4 sont identiques ou différents;
(c) un composé d'organoaluminium;
ce système étant caractérisé par un rendement de catalyseur dépassant 25 kg de produit polymère par gramme de catalyseur en une heure lorsque le rapport molaire Si/Ti tel que dérivé à partir du Si dans le composé (b) au Ti du composé (a) se situe dans l'intervalle 4-200.

12. Le système de la revendication 11 dans lequel le système est en outre caractérisé par un produit polymère dans lequel les matières solubles dans le xylène mesurées en dissolvant le polymère dans du xylène chaud, en refroidissant la solution à 0°C et en séparant par précipitation la forme isotactique, les produits solubles dans le xylène étant le pourcentage en poids du polymère qui est soluble dans le xylène froid, sont maintenus à 3,00% en poids ou moins du produit polymère alors que le rapport molaire Si/Ti se trouve dans l'intervalle de 4-200.

13. Le système de la revendication 11 dans lequel R_1 et R_4 sont des alkyles tertiaires de 4 à 13 atomes de carbone.

14. Le système de la revendication 13 dans lequel R_1 et R_4 sont des alkyles tertiaires de 4 à 7 atomes de carbone.

15. Le système de la revendication 11 dans lequel R_1 et R_4 sont identiques.

16. Le système de la revendication 15 dans lequel R_1 et R_4 sont des groupes t-butyles.

17. Le système de la revendication 11 dans lequel R_2 et R_3 sont choisis dans le groupe consistant en groupes méthyle, éthyle, propyle et butyle.

18. Le système de la revendication 11 dans lequel le catalyseur est prépolymérisé.

19. Le système de la revendication 11 dans lequel le composé d'organoaluminium est choisi dans le groupe consistant en trialkylaluminium, en dihalogénure d'alkylaluminium et en halogénure de dialkylaluminium.

20. Le système de la revendication 11 dans lequel le donneur d'électrons est choisi dans le groupe consistant en di-t-butyl-diméthoxysilane.

21. Le système de la revendication 18 dans lequel le composé d'organoaluminium est le triéthylaluminium.

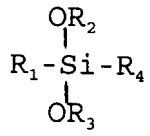
22. Un procédé de polymérisation d'oléfines, comprenant:

(a) choisir un composant de catalyseur de Ziegler-Natta habituel comprenant un composant de catalyseur

solide obtenu par (i) mettre en suspension un dialkoxy magnésium dans un hydrocarbure aromatique qui est liquide aux températures normales, (ii) mettre en contact le dialkoxy magnésium avec un halogénure de titane et mettre en outre en contact la composition résultante une deuxième fois avec l'halogénure de titane, et (iii) mettre en contact le dialkoxy magnésium avec un diester d'un acide aromatique dicarboxylique à un certain moment pendant le traitement avec l'halogénure de titane au cours de (ii);

(b) mettre en contact le composant de catalyseur avec un composé d'organoaluminium pour activer le catalyseur;

(c) mettre en contact ce catalyseur avec un donneur d'électrons externes soit simultanément soit après l'étape (b), ce donneur d'électrons étant décrit par la formule:



dans laquelle R_1 est un groupe alkyle contenant un atome de carbone tertiaire fixé à un atome de silicium; R_2 et R_3 sont chacun indépendamment un groupe alkyle ou aryle; et R_4 est un groupe alkyle avec un atome de carbone tertiaire fixé sur un atome de silicium; R_1 et R_4 sont identiques ou différents;

(d) prépolymériser ce catalyseur en mettant en contact une petite quantité de monomère avec ce catalyseur; et

(e) introduire ce catalyseur dans une zone de réaction de polymérisation contenant ce composé d'organoaluminium, ce donneur d'électrons et ce monomère.

23. Le procédé de la revendication 22 dans lequel ce composé de monomère est le triéthylaluminium.

24. Le procédé de la revendication 22 dans lequel R_1 et R_4 sont des alkyles tertiaires de 4 à 13 atomes de carbone.

25. Le procédé de la revendication 24 dans lequel R_1 et R_4 sont des alkyles tertiaires de 4 à 7 atomes de carbone.

26. Le procédé de la revendication 22 dans lequel R_1 et R_4 sont identiques.

27. Le procédé de la revendication 22 dans lequel R_1 et R_4 sont des groupes t-butyles.

28. Le procédé de la revendication 22 dans lequel ce monomère est le propylène.

29. Le procédé de la revendication 22 dans lequel ce donneur d'électrons est le di-t-butyl-diméthoxysilane.

30. Le procédé de la revendication 22 dans lequel ce procédé se caractérise par un rendement de catalyseur dépassant 25 kg de produit polymère par gramme de catalyseur en une heure avec un rapport molaire Si/Ti du donneur d'électrons de silicium et le catalyseur dans l'intervalle 4-200.

31. Le procédé de la revendication 22 dans lequel ce procédé se caractérise en ce qu'on produit un composé de polymère dans lequel les produits solubles dans le xylène mesurés en dissolvant le polymère dans du xylène chaud, en refroidissant la solution à 0°C et en séparant par précipitation la forme isotactique, les produits solubles dans le xylène étant un pourcentage du polymère qui est soluble dans le xylène froid, sont à 3,00% en poids ou moins du produit polymère.

32. Le procédé de la revendication 22 comprenant en outre l'addition d'un second monomère de façon à former un copolymère.